

## Statistical and Thermal Physics: Homework 19

Due: 8 May 2020

### 1 Maxwell speed distribution

The Maxwell speed distribution is

$$p_{\text{speed}}(v) = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-v^2 m/2kT}.$$

- Determine the most likely speed (the speed at which the probability is greatest).
- Show that the mean speed is

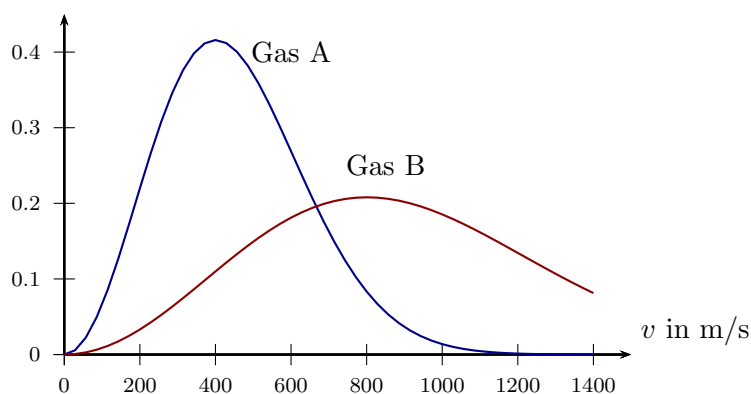
$$\bar{v} = \sqrt{\frac{8kT}{\pi m}}.$$

By what factor does this differ from the most likely speed?

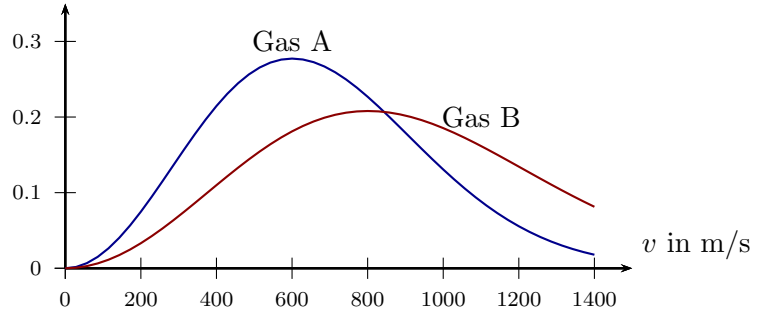
- As the temperature increases, what happens to the most likely speed and the mean speed?
- Determine the average kinetic energy for a single molecule using the Maxwell speed distribution and use the result to obtain an expression for the energy of an ideal monoatomic gas consisting of  $N$  such molecules.
- Consider nitrogen molecules ( $\text{N}_2$ ). Using the same axes, plot the Maxwell speed distribution for these molecules at 300 K and also 600 K. Indicate any differences in the graphs.

### 2 Maxwell speed distribution

- The distributions of speed for two gases, whose particles are the same, are provided. Describe as accurately as possible how the temperature of gas A is related to the temperature of gas B.



- b) The distributions of speed for two gases, whose temperatures are the same, are provided. Describe as accurately as possible how the mass of a molecule of gas A is related to the mass of a molecule of gas B.



### 3 Composition of Earth's atmosphere

The escape velocity of any particle from a location near Earth's surface is about 11 km/s and any particle with a speed larger than this will leave Earth. This notion can be used to understand Earth's atmosphere.

- a) Show that the probability with which a particle has a speed greater than  $v_{\min}$  is

$$\frac{4}{\sqrt{\pi}} \int_{v_{\min}/\sqrt{2kT/m}}^{\infty} u^2 e^{-u^2} du.$$

*Hint: Use the substitution  $u = v/\sqrt{2kT/m}$ .*

- b) Determine the probability with which a helium atom will have speed larger than Earth's escape velocity if the temperature is 300 K.
- c) Determine the probability with which a nitrogen molecule will have speed larger than Earth's escape velocity if the temperature is 300 K. By what factor is the helium molecule more likely to be able to escape Earth? Use the results to describe how the Earth has the atmosphere that it has.

*The integrals in parts b) and c) must be evaluated numerically. Wolfram Alpha and similar programs can do this.*

### 4 Thermal properties of a classical solid

In classical physics a solid can be modeled as a collection of distinguishable three dimensional harmonic oscillators, each with the same frequency,  $\omega$ . Any single oscillator has energy

$$E = \frac{\mathbf{p}^2}{2m} + \frac{1}{2}m\omega^2\mathbf{r}^2$$

where  $\mathbf{r}$  is the three dimensional position vector,  $\mathbf{p}$  is the three dimensional momentum vector and  $m$  is the mass of the oscillator. Suppose that the solid consists of  $N$  identical but distinguishable oscillators.

- a) Determine the partition function for the system of oscillators, assuming that it is in contact with an environment at temperature  $T$ .

- b) Show that the energy of the system is

$$\overline{E} = 3NkT$$

and determine the heat capacity of the system. This will yield the law of Dulong and Petit.

- c) At 298 K and 1 atm, the heat capacity of copper is 385.1 J/kg K, the heat capacity of aluminum is 897.1 J/kg K, and the heat capacity of iron is 449.3 J/kg K. How do these compare to the heat capacity, when converted to the correct units, as predicted by the law of Dulong and Petit?

## 5 Occupancy diagrams

- a) A system has two energy levels and contains three Bosons. Provide occupancy diagrams for all possible states of the system.
- b) A Fermi-Dirac system has four energy levels. Provide occupancy diagrams for all possible states of the system.

## 6 Bosons with zero chemical potential

Consider a system in which there is one energy level, with energy  $\epsilon$ . Suppose that the particles in the system are bosons,  $\epsilon > 0$ , and the chemical potential is  $\mu = 0$ .

- a) Determine the mean occupancy number, the mean energy and the heat capacity of the system as  $T \rightarrow 0$ .
- b) Determine the mean occupancy number, the mean energy and the heat capacity of the system as  $T \rightarrow \infty$ .
- c) Determine an expression for the temperature at which the mean energy is  $\overline{E} = \epsilon$ .

## 7 Fermion distributions

Consider a single system state with energy,  $\epsilon$ .

- a) Determine  $\overline{n}$  in the limits as  $T \rightarrow \infty$ . Does the result depend on the chemical potential? What does this imply about the likelihood of a Fermion occupying the state as the temperature becomes very large?
- b) Now consider the limit as  $T \rightarrow 0$ . There are two cases to consider. Determine  $\overline{n}$  in the limits as  $T \rightarrow 0$  if  $\epsilon > \mu$  and separately if  $\epsilon < \mu$ . What does this imply about the likelihood of a Fermion occupying the state as the temperature becomes very small?
- c) Now suppose that  $T$  is fixed and consider the mean occupation number as a function of energy. Determine  $\overline{n}$  for  $\epsilon = \mu$ .

The next exercises aim to plot the Fermi-Dirac distribution as a function of  $\epsilon$  for various temperatures.

d) Show that for Fermions

$$\bar{n} = \frac{1}{e^{(\epsilon'-1)\alpha} + 1}$$

where  $\epsilon' := \epsilon/\mu$  is a rescaled energy variable and  $\alpha := \mu/kT$  contains information about temperature. Suppose that  $\mu$  is fixed. Plot, using the same axes,  $\bar{n}$  versus  $\epsilon'$  in the range  $0 \leq \epsilon' \leq 2$ , for the following temperatures:  $T = 0.01\mu/k$ , (lower temperature),  $T = 0.2\mu/k$ ,  $T = 1\mu/k$ ,  $T = 10\mu/k$  (even higher temperature).

e) These graphs should reveal the behavior of Fermions as temperature changes. Suppose that there are many energy states in the system, each with distinct energies. At very low temperatures how will the states be populated? Which are very likely to contain a particle, which are very unlikely to contain a particle? At very high temperatures, how will the states be populated?

a) We need to maximize

$$f(v) = v^2 e^{-v^2 \alpha}$$

where  $\alpha = m/2kT$

$$\text{Then } \frac{df}{dv} = 0 \Leftrightarrow 2v e^{-v^2 \alpha} + v^2 (-2v\alpha) e^{-v^2 \alpha} = 0$$

$$\Leftrightarrow v - \alpha v^3 = 0 \Leftrightarrow v(1 - \alpha v^2) = 0$$

$$\Leftrightarrow v = 0 \text{ or } v = \frac{1}{\sqrt{\alpha}}$$

Thus the maximum occurs when

$$v = \frac{1}{\sqrt{m/2kT}} \Rightarrow v_{\max} = \sqrt{\frac{2kT}{m}}$$

$$b) \quad \bar{v} = \int_0^{\infty} v p_{\text{speed}}(v) dv$$

$$= 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \int_0^{\infty} v^3 e^{-v^2 m/2kT} dv$$

$$\frac{1}{2(m/2kT)^2} = \frac{2k^2 T^2}{m^2}$$

$$= 4\pi \left( \frac{1}{2\pi} \right)^{3/2} \left( \frac{m}{kT} \right)^{3/2} \left( \frac{kT}{m} \right)^2 2 = \left( \frac{2^3}{2^{3/2}} \right) \frac{1}{\sqrt{\pi}} \left( \frac{kT}{m} \right)^{1/2}$$

$$\Rightarrow \bar{v} = \sqrt{\frac{8kT}{\pi m}}$$

$$\text{Then } \frac{\bar{v}}{v_{\max}} = \frac{\sqrt{8/\pi}}{\sqrt{2}} = \sqrt{\frac{4}{\pi}}$$

c) they both increase.

d)  $K = \frac{1}{2} M V^2$

1.

So  $\bar{K} = \frac{1}{2} m \bar{V}^2$

For one  
molecule

Need  $\bar{V}^2 = \int_0^{\infty} v^2 p(v) dv$   $V^4 ??$

$$= 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \int_0^{\infty} v^2 e^{-v^2 m/2kT} dv$$

$$= \frac{3}{8} \frac{\sqrt{\pi}}{(m/2kT)^{5/2}}$$

$$= 4\pi \left( \frac{1}{2\pi} \right)^{3/2} \frac{3}{8} \sqrt{\pi} 2^{+5/2} \frac{kT}{m}$$

$$= \frac{4}{\sqrt{8}} \frac{3}{8} \sqrt{32} \frac{kT}{m}$$

$$= \frac{13}{2} \sqrt{4}$$

$$= 3 \frac{kT}{m}$$

So  $\bar{K} = \frac{1}{2} m \bar{V}^2$

$$\bar{K} = \frac{3}{2} kT$$

For  $N$  molecules  $\bar{K} = \frac{3}{2} NkT$

e) Here  $m = \frac{2 \times 14 \text{ g/mol}}{6.02 \times 10^{23} \text{ particles/mol}} = 4.65 \times 10^{-23} \text{ g}$

$$m = 4.65 \times 10^{-26} \text{ kg}$$

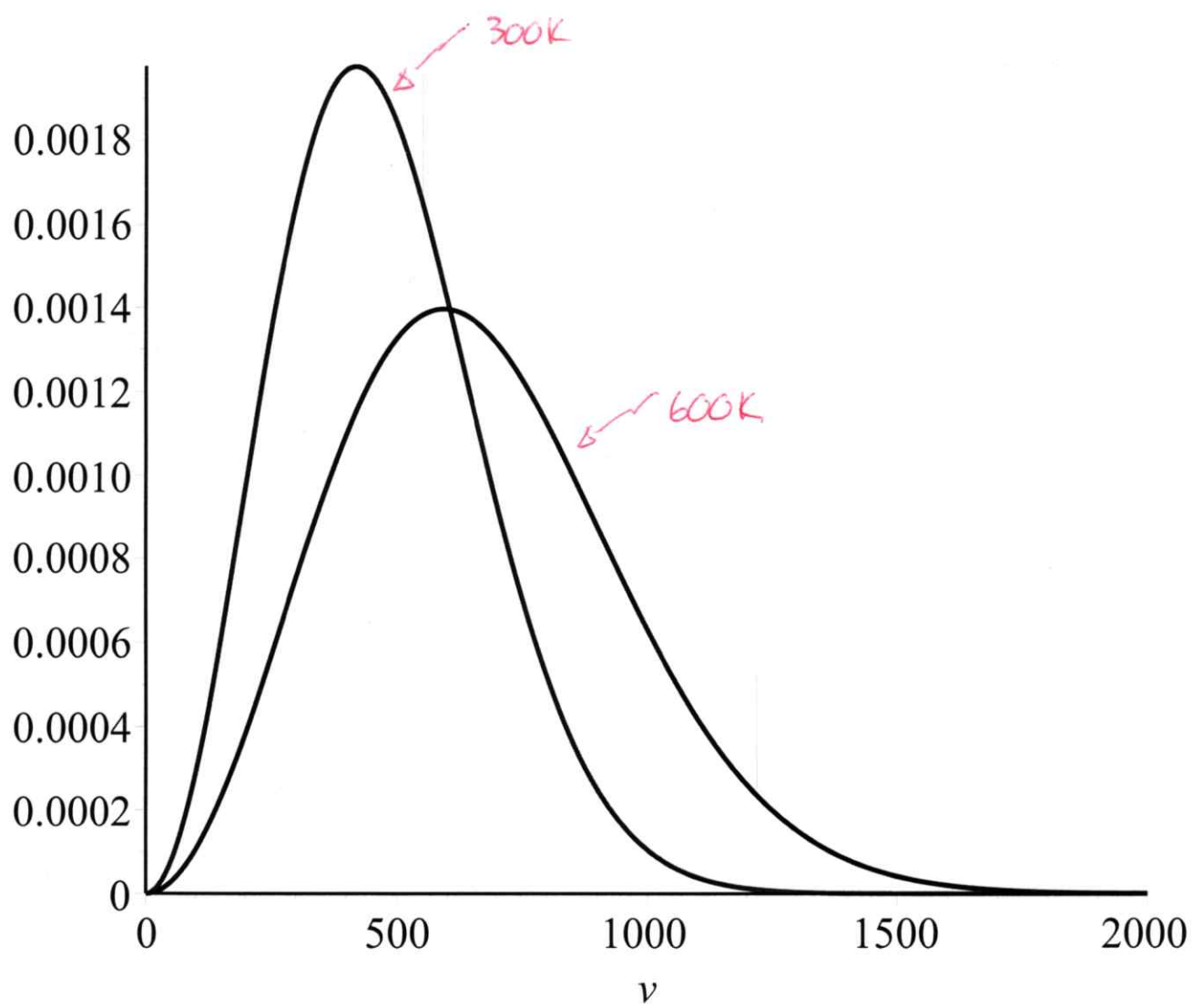
So  $\frac{m}{2kT} = \frac{4.65 \times 10^{-26} \text{ kg}}{2 \times 1.38 \times 10^{-23} \text{ J/K } T} = 0.0017/T$

Then  $P_{\text{speed}}(v) = 4\pi \left( \frac{0.0017}{\pi T} \right)^{3/2} v^2 e^{-v^2 0.0017/T}$

For  $T=300\text{K}$   $P_{\text{speed}}(v) = \frac{4}{\sqrt{\pi}} \left( \frac{0.0017}{300} \right)^{3/2} v^2 e^{-v^2 0.0017/300}$

$T=600\text{K}$   $P_{\text{speed}}(v) = \frac{4}{\sqrt{\pi}} \left( \frac{0.0017}{600} \right)^{3/2} v^2 e^{-v^2 0.0017/600}$

At higher temps the distribution is flatter and peaks further right.





Note the ~~max~~ most likely speed is

$$V = \sqrt{\frac{2kT}{m}}$$

a)  $V_A = \frac{1}{2} V_B$

$$\Rightarrow \sqrt{\frac{2kT_A}{m}} = \frac{1}{2} \sqrt{\frac{2kT_B}{m}} \Rightarrow \frac{2kT_A}{m} = \frac{1}{4} \frac{2kT_B}{m} \Rightarrow T_A = \frac{1}{4} T_B$$

b)  $V_A = \frac{6}{8} V_B = \frac{3}{4} V_B$

$$\Rightarrow \sqrt{\frac{2kT}{m_A}} = \frac{3}{4} \sqrt{\frac{2kT}{m_B}} \Rightarrow \frac{2kT}{m_A} = \frac{9}{16} \frac{2kT}{m_B}$$

$$\Rightarrow m_A = \frac{16}{9} m_B$$

$$a) \quad \text{prob}(v > v_{\min}) = \int_{v_{\min}}^{\infty} P_{\text{speed}}(v) dv$$

$$= 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \int_{v_{\min}}^{\infty} v^2 e^{-v^2 m / 2kT} dv$$

$$\text{let } u = v / \sqrt{2kT/m} \quad \Rightarrow \quad du = dv / \sqrt{2kT/m}$$

$$\checkmark$$

$$\Rightarrow dv = \sqrt{2kT/m} du$$

$$v = u \sqrt{2kT/m}$$

$$\text{So } \text{prob}(v > v_{\min}) = \int_{v_{\min}/\sqrt{2kT/m}}^{\infty} u^2 (2kT/m) e^{-u^2 \sqrt{2kT/m}} du \times 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2}$$

$$= \left( \frac{2kT}{m} \right)^{3/2} 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \int_{v_{\min}/\sqrt{2kT/m}}^{\infty} u^2 e^{-u^2} du$$

$$= \frac{4}{\sqrt{\pi}} \int_{\underbrace{v_{\min}/\sqrt{2kT/m}}_{u_{\min}}}^{\infty} u^2 e^{-u^2} du$$

$$b) \quad m = 4.0 \times 10^{-3} \text{ kg} / 6.02 \times 10^{23} = 6.64 \times 10^{-27}$$

$$v_{\min} = 11 \times 10^3 \text{ m/s}$$

$$T = 300 \text{ K}$$

$$\Rightarrow u_{\min} = v_{\min} / \sqrt{2kT/m} = 9.85 \Rightarrow \text{prob} = \frac{4}{\sqrt{\pi}} \int_{9.85}^{\infty} u^2 e^{-u^2} du = 8.1 \times 10^{-42}$$

c)  $m = 4.65 \times 10^{-26} \text{ kg}$

$T = 10300 \text{ K}$

$\Rightarrow u_{\min} = 26.1$

$\Rightarrow \text{prob} = \frac{4}{\sqrt{\pi}} \int_{26.1}^{\infty} u^2 e^{-u^2} du = 3.38 \times 10^{-294}$

This is a factor of  $\frac{3.38 \times 10^{-294}}{8.1 \times 10^{-42}} \sim 4 \times 10^{-253}$

smaller than for He... So Helium is far more likely to escape.

Hot

a) 
$$Z = C(N) \int e^{-(\vec{p}_1^2 + \dots + \vec{p}_N^2) \beta / 2m} e^{-(\vec{r}_1^2 + \dots + \vec{r}_N^2) \beta m \omega^2 / 2} d\vec{p}_1 \dots d\vec{p}_N d\vec{r}_1 \dots d\vec{r}_N$$

But 
$$\int e^{-\vec{p}_1^2 \beta / 2m} d\vec{p}_1 = \int_{-\infty}^{\infty} e^{-p_{1x}^2 \beta / 2m} dp_{1x} \int_{-\infty}^{\infty} e^{-p_{1y}^2 \beta / 2m} dp_{1y} \dots$$

$$= \left( \sqrt{\frac{2\pi m}{\beta}} \right)^3 = (2\pi m kT)^{3/2}$$

Similarly 
$$\int e^{-\vec{r}_1^2 \beta m \omega^2 / 2} d\vec{r}_1 = \left( \sqrt{\frac{2\pi}{m \omega^2 \beta}} \right)^3 = \left( \frac{2\pi kT}{m \omega^2} \right)^{3/2}$$

Thus 
$$Z = C(N) \left[ \frac{4\pi^2}{\beta^2 \omega^2} \right]^{3N/2} = C(N) \left[ \frac{2\pi}{\beta \omega} \right]^{3N}$$

b) 
$$\bar{E} = - \frac{\partial}{\partial \beta} \ln Z = - \frac{\partial}{\partial \beta} \left\{ \ln C(N) + \frac{3N}{2} \ln \left( \frac{4\pi^2}{\beta^2 \omega^2} \right) \right\}$$

$$= \frac{3N}{2} \beta \times 2 = 3N\beta \Rightarrow \bar{E} = 3NkT$$

$$C = \frac{\partial \bar{E}}{\partial T} = 0$$

$$C = 3Nk$$

c) For each we have C per kg. Part b gives C for number of particles. For one mole  $N = N_A$  and we get

For one mole b)  $\Rightarrow C = 3N_A k = 8.31 \text{ J/mol} \cdot \text{K} \times 3 = 24.9 \text{ J/mol} \cdot \text{K}$

We need to convert the data to J/mol.

$\boxed{\text{Cu}}$   $1 \text{ mol} = 63.55 \text{ g} \Rightarrow 1 \text{ kg} = 15.7 \text{ mol} \Rightarrow C = \frac{385.1 \text{ J/kg} \cdot \text{K}}{15.7 \text{ mol/kg}} = 24.5 \text{ J/mol} \cdot \text{K}$

$\boxed{\text{Al}}$   $1 \text{ mol} = 26.98 \text{ g} \Rightarrow 1 \text{ kg} = 37.1 \text{ mol} \Rightarrow C = \frac{897.1 \text{ J/kg} \cdot \text{K}}{37.1 \text{ mol/kg}} = 24.2 \text{ J/mol} \cdot \text{K}$

$\boxed{\text{Fe}}$   $1 \text{ mol} = 55.85 \text{ g} \Rightarrow 1 \text{ kg} = 17.9 \text{ mol} \Rightarrow C = \frac{449.3 \text{ J/kg} \cdot \text{K}}{17.9 \text{ mol/kg}} = 25.1 \text{ J/mol} \cdot \text{K}$

$\boxed{\text{Close!}}$

a)

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b)

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For Bosons

$$\bar{n}(\epsilon) = \frac{1}{e^{(\epsilon - \mu)\beta} - 1}$$

and

$$\bar{E} = \sum \epsilon \bar{n}(\epsilon)$$

If  $\mu = 0$  then

$$\bar{n} = \frac{1}{e^{\epsilon\beta} - 1}$$

If there is only one energy level then

$$\bar{E} = \epsilon \bar{n} = \frac{\epsilon}{e^{\epsilon\beta} - 1} \quad C = \frac{d\bar{E}}{dT} = -\frac{\epsilon e^{\epsilon\beta} \left(-\frac{\epsilon}{kT^2}\right)}{(e^{\epsilon\beta} - 1)^2} = \frac{\epsilon}{kT^2} \frac{e^{\epsilon\beta}}{(e^{\epsilon\beta} - 1)^2}$$

a) As  $T \rightarrow 0$   $\beta \rightarrow \infty \Rightarrow e^{\epsilon\beta} \rightarrow \infty \Rightarrow$   $\bar{n} \rightarrow 0$   $C \rightarrow 0$

$$\bar{E} \rightarrow 0$$

b) As  $T \rightarrow \infty$   $\beta \rightarrow 0 \Rightarrow e^{\epsilon\beta} \rightarrow 1 \Rightarrow \bar{n} \rightarrow \infty$   $C \rightarrow \frac{\epsilon}{kT^2} \frac{1}{\epsilon/kT} = \frac{1}{T}$   
 $e^{\epsilon\beta} \rightarrow 1 + \epsilon/kT \Rightarrow \bar{E} \rightarrow \infty \rightarrow 0$   
 $\Rightarrow \bar{E} \rightarrow kT$

c) Need  $\epsilon = \frac{\epsilon}{e^{\epsilon\beta} - 1} \Rightarrow e^{\epsilon/kT} = 2 \Rightarrow \epsilon/kT = \ln 2$

$$\Rightarrow T = \frac{\epsilon}{k \ln 2}$$

For Fermions

$$\bar{n} = \frac{1}{e^{(\epsilon - \mu)\beta} + 1} = \frac{1}{e^{(\epsilon - \mu)/kT} + 1}$$

a) As  $T \rightarrow \infty$   $e^{(\epsilon - \mu)/kT} \rightarrow e^0 \rightarrow 1 \Rightarrow \bar{n} \rightarrow 1/2$

It is just as likely that the state will be occupied as not. To see this mathematically, let  $p$  = probability that state is occupied. Then

$$\begin{aligned}\bar{n} &= \text{prob occupied} \times 1 + \text{prob unoccupied} \times 0 \\ &= p = 0 \quad p = 1/2\end{aligned}$$

b) If  $\epsilon > \mu$  then  $(\epsilon - \mu)/kT \rightarrow \infty$  and  $\bar{n} \rightarrow 0$

If  $\epsilon < \mu$  then  $(\epsilon - \mu)/kT \rightarrow -\infty$  and  $\bar{n} \rightarrow 1$

In the first case zero probability that state is occupied

In the second case certainty that the state is occupied

c)  $\bar{n} = \frac{1}{e^0 + 1} = \frac{1}{2} \Rightarrow \bar{n} = 1/2$

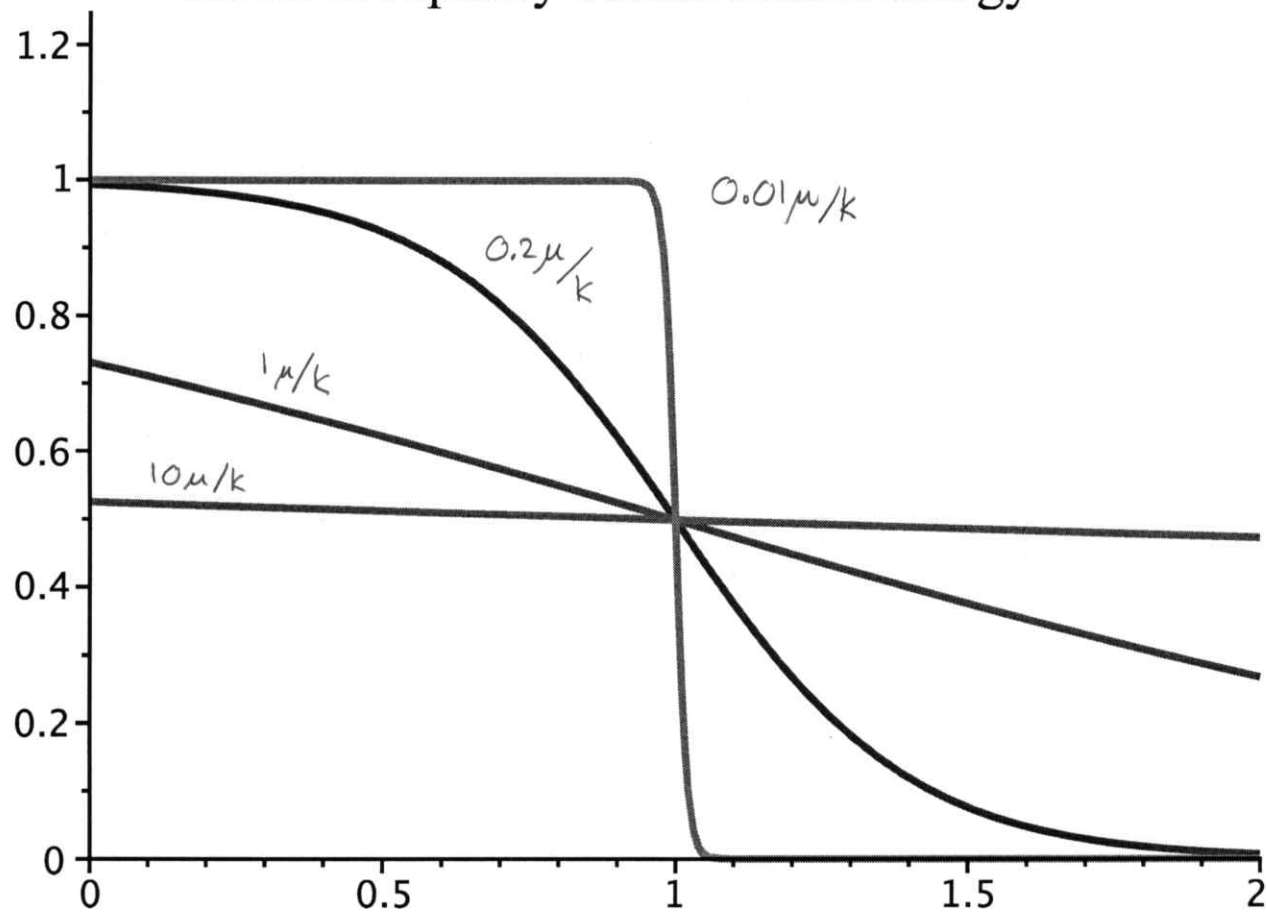
As  $\epsilon \rightarrow 0$   $\bar{n} \rightarrow \frac{1}{e^{-\mu/kT} + 1}$  As  $\epsilon \rightarrow \infty$   $\bar{n} \rightarrow \frac{1}{\infty} = 0$

d)  $\bar{n} = \frac{1}{e^{(\epsilon - \mu - 1)\beta} + 1} = \frac{1}{e^{(\epsilon - 1)\alpha} + 1}$

Then

$T$	$0.01\mu/k$	$0.2\mu/k$	$1\mu/k$	$10\mu/k$
$\alpha$	100	5	1	0.10

Mean occupancy versus scaled energy





e) It's always when  $\epsilon = \mu$

f) At very low temperatures all states with energy  $\epsilon < \mu$  will be populated with one Fermion

no states with energy  $\epsilon > \mu$  will be populated.

At very high temperatures - each state is just as likely to be populated as it is to be unpopulated.